PCT

International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [6]: C23C 14/08, 14/34, C04B 35/46

A1

(11) International Publication Number: WO 97/25450

(43) International Publication Date: 17 July 1997 (17.07.97

(21) International Application Number: PCT/EP97/00021

(22) International Filing Date: 3 January 1997 (03.01.97)

(30) Priority Data:
9600210.0 5 January 1996 (05.01.96) GB

(71) Applicant *(for all designated States except US)*: BVBA VANDERSTRAETEN E [BE/BE]; E3 Laan 75-79, B-9800 Deinze (BE).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: VANDERSTRAETEN, Johan, Emile, Marie [BE/BE]; Gavergrachstraat 18, B-9031 Drongen (BE).

(74) Agent: BOULT WADE TENNANT; 27 Furnival Street, London EC4A 1PQ (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG)

Published
With international search report.

(54) Title: PROCESS FOR COATING A SUBSTRATE WITH TITANIUM DIOXIDE

(57) Abstract

A process for coating a substrate surface with titanium dioxide, which process comprises the D.C. plasma sputtering and/or mid-frequency sputtering from a sputtering target which comprises sub-stoichiometric titanium dioxide, TiO_x, where x is below 2.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic			SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

PROCESS FOR COATING A SUBSTRATE WITH TITANIUM DIOXIDE

The present invention relates to an improved process for coating a substrate surface with titanium dioxide.

Sputtered coatings of various oxides (e.g. silica) and nitrides (e.g. silicon nitride) are used to form optical coatings showing interesting properties on a number of substrates. Known applications include low emissivity films on window glasses, cold mirrors on reflectors, enhanced mirrors for photocopiers and anti-reflective coatings on picture glass or TV screens. These coatings are usually made of stacks of several different layers with different refractive indices, preferably of low and high refractive index, to produce optical filters. For anti-reflective coatings it is preferred to combine two materials showing the highest and the lowest possible refractive indices. Such materials are titania and silica. Another advantage of these materials is their durability. For low emissivity films on window glasses it is preferred to combine a silver layer with a high refractive index material to dereflect the silver which improves light transmission.

Titanium dioxide coatings have a high refractive index and can thus be used to provide coatings of a high refractive index or to provide the high refractive index coatings in optical stacks. The existing process for producing titanium dioxide coatings comprises using titanium metal as the sputtering target and using oxygen as a component of the plasma gas. The titanium is thus converted to titanium dioxide during the sputtering process.

Although satisfactory coatings of titanium dioxide can be produced, the rate of deposition is very slow and much slower than coating with zinc oxide and/or tin oxide. The stability of the sputtering process and the arc rate are both very dependent upon the conductivity of the target, particularly at high power levels.

As a substitute for titanium dioxide it has been suggested to use alternative materials such as niobium oxide. Whilst it is possible to coat a substrate with niobium oxide using a niobium metal target at slightly higher speeds than the equivalent process using titanium, niobium is very expensive.

JP-A-62-161945 describes a method of manufacturing a ceramic sputtering target in which a ceramic material consisting mainly of ZrO_2, TiO_2, SiO_2, Ta_2O_3, Al_2O_3, Fe_2O_3 or a compound of these materials, is sprayed using a water plasma spray to produce a formed body which may be used as a sputtering target. The sputtering target is used for high frequency sputtering of non-conductive target material.

JP-A-1-118807 describes a method for manufacturing titanium oxide thin films in which a target comprising titanium, titanium monoxide (TiO), or titanium dioxide (TiO_2) is used as a sputtering target and the target sputtered in a mixture of argon and oxygen using high frequency power density for example of 500W.

There is, however, still a need for an improved process for coating titanium dioxide onto substrate materials. We have now surprisingly discovered that titanium dioxide can be sputtered from a target comprising sub-stoichiometric titanium dioxide of low resistivity of less than 1 ohm.cm, preferably less than 0.1 ohm.cm to provide coatings on a substrate either of sub-stoichiometric titanium dioxide, or

titanium dioxide, depending upon the sputtering conditions.

Accordingly, the present invention provides a process for coating a substrate surface with titanium dioxide, which process comprises the D.C. plasma sputtering and/or mid-frequency sputtering from a sputtering target which comprises sub-stoichiometric titanium dioxide, TiO_x, where x is below 2, and which has a resistivity of below 1 ohm.cm.

Sub-stoichiometric titanium dioxide, TiO_x, where x is below 2 and generally is in the range of from 1.55 to 1.95 is known in the art. It is a form of titanium dioxide which is conductive. Preferably the sub-stoichiometric titanium dioxide used in the present invention has a resistivity of below 0.1 ohm.cm.

The sputtering target which is used in the process of the present invention comprises sub-stoichiometric titanium dioxide, TiO_x coated onto a target base, such as a backing tube or plate, for example a target base of an electrically conductive material, for example stainless steel or titanium metal, aluminium or copper. Because the sub-stoichiometric titanium dioxide is conductive, D.C. plasma sputtering and/or mid-frequency sputtering, such as the Twin-Mag System may be used. D.C. plasma sputtering is, however, preferred. The target may be of any type known in the art, for example a rotatable target or a flat magnetron target.

The sputtering target used in the process of the present invention may be prepared by plasma spraying titanium dioxide, optionally together with niobium oxide, onto a target base in an atmosphere which is oxygen deficient and which does not contain oxygen-containing compounds, the target base being coated

with TiO_x, where x is below 2, which is solidified under conditions which prevent the sub-stoichiometric titanium oxide from combining with oxygen. During the plasma spraying process, the action of the plasma on the titanium dioxide causes the titanium dioxide to lose some oxygen atoms from its lattice preferably from the surface of the particles. The titanium dioxide is converted into the sub-stoichiometric form, i.e. non-stoichiometric oxygen deficient titania

The sputtering from the sub-stoichiometric titanium dioxide, TiO_x target is preferably carried out using as the plasma gas argon, a mixture of argon and oxygen, a mixture of nitrogen and argon, or a mixture of nitrogen and oxygen. If the plasma gas does not contain oxygen, e.g. if pure argon is used, then the coating will comprise sub-stoichiometric titanium dioxide. The coating obtained is not completely transparent and possesses some conductivity. If, however, the plasma gas contains oxygen then the sub-stoichiometric form of titanium dioxide is converted during the sputtering process into the transparent form which is stoichiometric or substantially stoichiometric and has a high refractive index. The degree of transparency will depend upon the amount of oxygen contained in the plasma gas. A preferred gas mixture to form transparent titanium dioxide as the coating comprises 70-90% by volume argon and 30-10% by volume of oxygen.

The substrate which is coated according to this process may comprise, for example, optical glass, the screen of a cathode ray tube, such as a TV screen, cold mirrors, low-emissivity glasses, architectural glasses, anti-reflective panels, or flexible films such as oxygen barrier films.

The use of the target of the present invention

avoids any avalanche effect of titania towards the metallic state or poisoned oxygen state. There is no need for a sophisticated gas control system or plasma monitoring equipment. The target can be easily operated and controlled to produce stoichiometric or non-stoichiometric films of any level of sub-stoichiometry. By operating the target in a slightly oxygen deficient sputtering process, a high refractive index film can be obtained which is important for optical coatings. Depending on the sputtering parameters, amorphous or crystalline films can be formed with a rutile or anatase structure. Rutile films have improved optical, mechanical and electrical properties. When the sub-stoichiometric titanium dioxide is sputtered under conditions such that the coating is formed comprises stoichiometric titanium dioxide, the coating is essentially transparent and colourless.

Although films coated with stoichiometric titanium dioxide, for example for use in the packaging industry, have good oxygen barrier properties, they are statically loaded which is particularly disadvantageous especially for the packaging of powdered products, such as coffee.

When the coating formed from the sub-stoichiometric titanium dioxide sputtering targets is also sub-stoichiometric titanium dioxide, it has a reduced transparency and slightly blue colour but is conductive and thus possesses anti-static properties having an electrical resistivity of above 3×10^5 ohm.cm. Accordingly, films coated with non-stoichiometric titanium dioxide not only have good oxygen barrier properties, but also possess particularly good anti-static properties which makes them particularly suitable for packaging applications,

particularly in the food industry. A further advantage of films coated with sub-stoichiometric titanium dioxide is that the coatings possess good flexibility which even after excessive bending and creasing retain their oxygen barrier properties. Although the films have a slight blue colour this does not detract from the potential use of the product in the food industry, the blue colour providing a "fresh" look to the product. As barrier films for water vapour and oxygen, there is an improvement when compared with the prior art titanium dioxide coated films of five fold for water vapour and three fold for oxygen.

The main advantage of the present invention is that from the sub-stoichiometric titanium dioxide targets used in the present invention the rate of sputtering is increased by a factor of about ten as compared to sputtering from a titanium metal target, thus making the process industrially attractive. Furthermore, the sputtering process is very stable with little or no arcing occurring.

The present invention will be further described with reference to the following Examples.

EXAMPLE 1 (Comparative)

A rotatable target comprising a tube of titanium metal of diameter 133mm and length 800mm was used to sputter titanium metal onto a glass plate placed at a distance of 18cm from the target. The sputtering was carried out at a power level of 35kW (80A, 446V) under a pressure of 5×10^{-3} mBar of argon as the plasma gas.

After 3½ minutes a layer of titanium metal 18000 Angstroms in thickness as measured by a profilometer had been deposited upon the glass plate.

EXAMPLE 2 (Comparative)

The procedure of Example 1 was repeated but substituting a mixture of 80% O_2 and 20% Ar as the primary plasma gas to replace the argon primary plasma gas of Example 1. The sputtering was carried out at a power level of 45kW (97A, 460V) under a pressure of 4.5×10^{-3} mBar. Using a titanium metal target as described in Example 1 a titanium dioxide layer of thickness 1500 Angstroms was deposited on a glass plate place above the target in 3½ minutes.

EXAMPLE 3

A rotatable target comprising a tube of stainless steel of diameter 133mm and length 800mm was coated with sub-stoichiometric titanium dioxide, TiO_x, where x is below 2 as hereinbefore described by plasma spraying titanium dioxide onto the target using argon as the primary plasma gas and hydrogen as the secondary plasma gas. 72 litres (60% argon, 40% hydrogen) were used. The power level was 45kW (455A, 96V).

This target was then used as a sputtering target in the manner as described in Example 1. Using argon as the primary plasma gas the sputtering was carried out at a power level of 45kW (97A, 460V) under a pressure of 5.4×10^{-3} mBar Ar. A dark blue semi-transparent layer of sub-stoichiometric titanium dioxide, TiO_x, of thickness 14000 Angstroms was deposited on a glass plate placed above the target in 3½ minutes. The sputtering proceeded smoothly without significant arcing.

EXAMPLE 4

A rotatable target prepared as described in Example 3 was used as a sputtering target in the manner as described in Example 3 using a mixture of 75% Ar and 25% O_2 as the plasma gas. The sputtering was carried out at a power of 45kW (95A, 473V) under a pressure of 5×10^{-3} mBar. A clear transparent coating of stoichiometric titanium dioxide of thickness 12500 Angstroms was deposited on a glass plate placed above the target in 3½ minutes. The sputtering proceeded smoothly without significant arcing.

EXAMPLE 5 (Comparative)

A rotatable target was prepared as described in Example 3 by using pure argon (40 litres) at a power level of 34 kW (820A, 42V). The electrical conductivity of the target was ten times inferior to that of Example 3. Sputtering from the target was difficult due to arcing. The process was not stable enough to produce samples.

CLAIMS:

1. A process for coating a substrate surface with titanium dioxide, which process comprises the D.C. plasma sputtering and/or mid-frequency sputtering from a sputtering target which comprises substoichiometric titanium dioxide, TiO_x, where x is below 2 and which has a resistivity of below 1 ohm.cm.

2. A process as claimed in claim 1 wherein the sputtering from the target is carried out using as the plasma gas argon, or a mixture or argon and nitrogen, whereby the coating formed on the substrate surface comprises sub-stoichiometric titanium dioxide, TiO_x, where x is below 2.

3. A process as claimed in claim 1 wherein the sputtering for the target is carried out using as the plasma gas a mixture of argon and oxygen, or a mixture of nitrogen and oxygen, whereby the coating formed on the substrate surface comprises stoichiometric or substantially stoichiometric titanium dioxide.

4. A process as claimed in claim 3 wherein the plasma gas comprises 70 to 90% by volume argon and 30 to 10% by volume oxygen.

5. A process as claimed in any one of claims 1 to 4 wherein the substrate which is coated is optical glass, the screen of a cathode ray tube, a cold mirror, a low emissivity glass, an architectural glass, an anti-reflective panel glass, the screen of a cathode ray tube, a flexible film or a water vapour and oxygen barrier film.

6. A process as claimed in any one of the preceding claims wherein the sub-stoichiometric titanium dioxide has a resistivity of less than 0.1 ohm.cm.

7. A substrate which has been coated by a process as claimed in any one of claims 1 to 6.

8. A substrate as claimed in claim 7 which is a flexible film coated with sub-stoichiometric titanium dioxide, TiO_x, which has anti-static properties.

9. A substrate as claimed in claim 7 wherein the coating is sub-stoichiometric titanium dioxide, TiO_x, which has a rutile crystalline structure.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C14/08 C23C14/34 C04B35/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 001, 31 January 1996 & JP 07 233469 A (ASAHI GLASS CO LTD), 5 September 1995, see abstract; tables 1,2 ---	1-5,7
A	DATABASE WPI Section Ch, Week 8925 Derwent Publications Ltd., London, GB; Class L03, AN 89-181603 XP002010492 & JP 01 118 807 A (HITACHI LTD) , 11 May 1989 see abstract -----	1-9

☐ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
10 April 1997	17.04.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Patterson, A